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Zn Speciation in Two Fe-Mn Banded Systems

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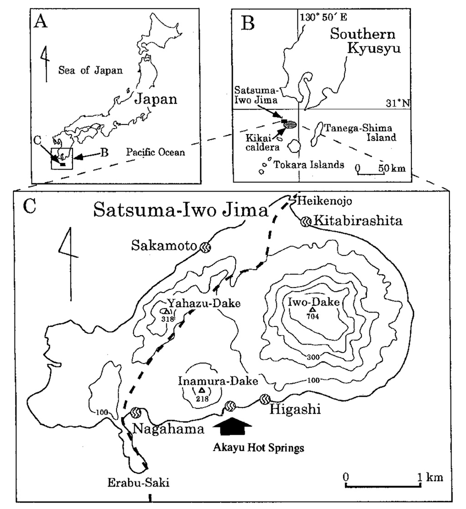
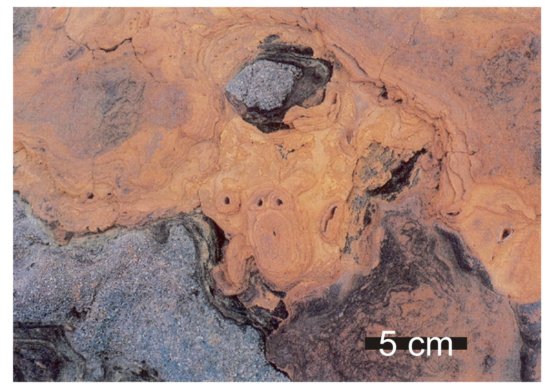
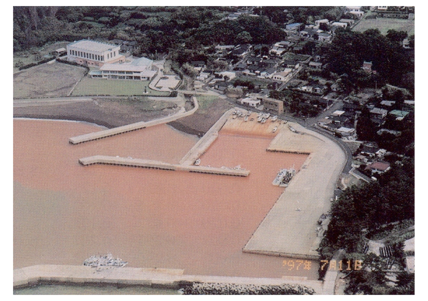
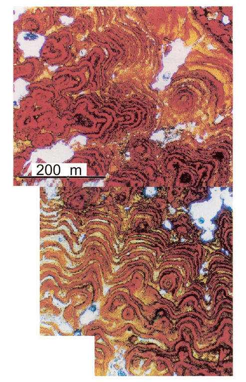
What we did: Micro-XRF and micro-EXAFS at Zn and Mn on two Fe-Mn banded systems: looking at Fe/Mn/Zn distribution and Mn and Zn speciation.

Why we care: Fe-Mn banded systems are ubiquitous, occurring in soils, shallow oceans, deep oceans, hotsprings,...
They have similarities despite differences in formation. Some are biogenic, some not.
Question: Are there common themes? How transferrable is the structural information? Does it matter if bacteria were involved?

Samples

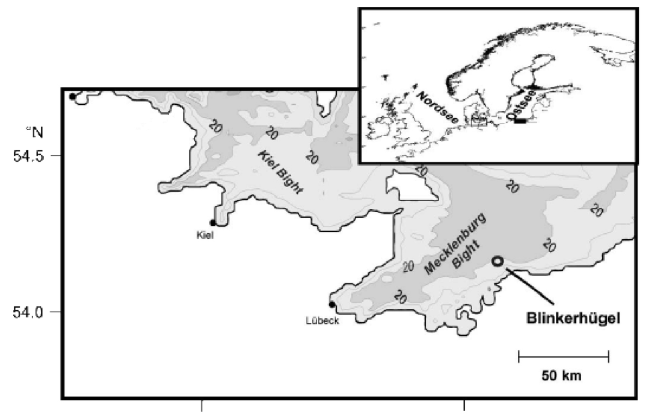
Bacterial mat from Japan

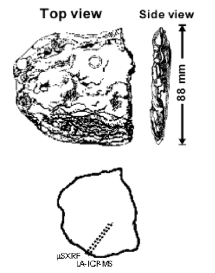



Ref: Tazaki, K., *Clays and Clay Minerals* **48**,511-520 (2002)

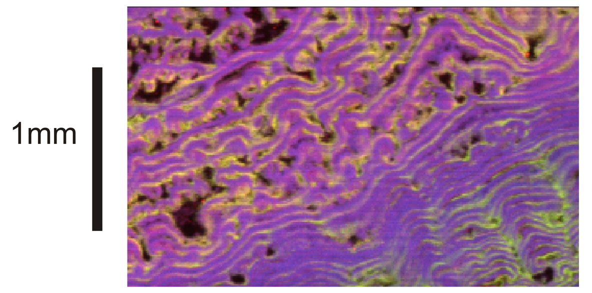
Shallow-ocean nodule from Baltic





Ref: S. Hlawatsch, T. Neumann, C. M. G. van den Berg, M. Kersten, J. Harff, E. Suess, *Marine Geology* **182**,373-387(2002)

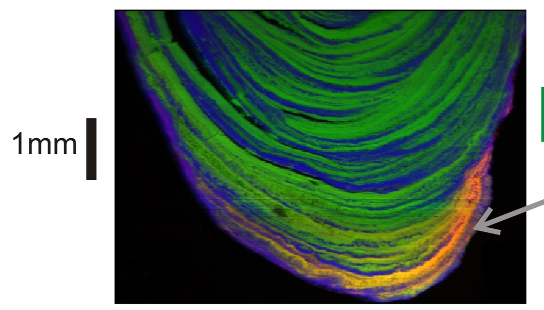
Elemental maps



Bacterial mat from hotsprings at seashore
Zn is at natural abundance.

Tricolor elemental maps

Mn Fe Zn



Zn at rim is anthropogenic and was deposited only when outer layers were growing.

Similarities: Fe/Mn alternation due to oscillating chemistry. Zn prefers Mn to Fe.

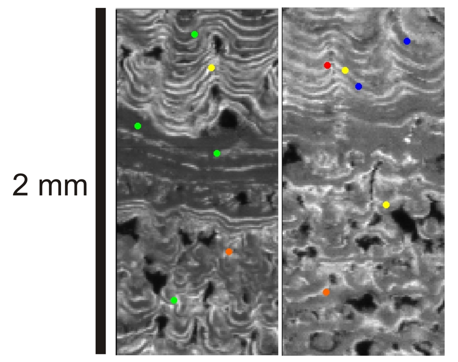
Differences: Japanese sample has Zn everywhere; Baltic one mostly in rim,due to natural/anthropogenic Zn source.

Zn less segregated in Japan sample than Baltic.

Zn XANES: Japan

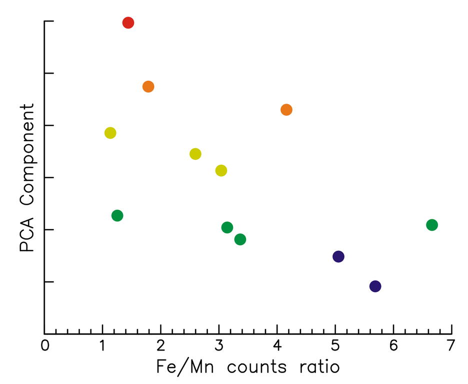
Look at different points and analyze by XANES. Use PCA to characterize spectra.

Colored points mark where spectra were taken. Colors match those on XANES and PCA plots



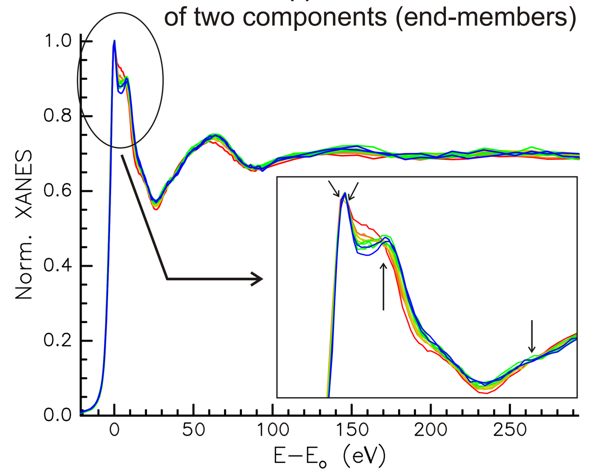
Mn map (high Mn=light)

Results from Principal Components Analysis
Points colored according to PCA component strength



Zn extended XANES from spots shown above

Isosbestic points (arrowed in insert) show that data approximates linear combinations of two components (end-members)

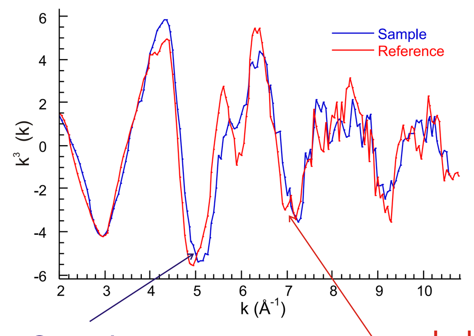


Results: XANES shows a clear variation with location on sample. Data are approximately described as linear combinations of two end-members, with fractions (related to PCA 2nd component strength) correlated with Fe/Mn ratio.

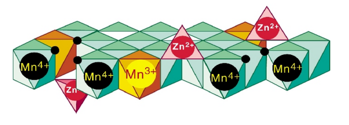
This is consistent with EXAFS picture of competing sorption on hydrous ferric oxides and phyllomanganates.

Zn EXAFS: Baltic

Zn and Mn EXAFS and XANES is uniform over area tested, unlike Japan sample.

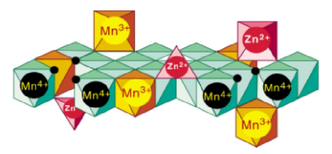


Sample



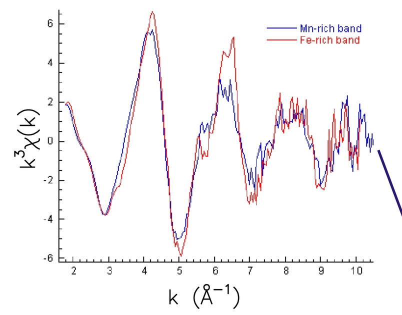
Zn sorbed on turbostratic birnessite: Tetrahedral Zn and some Mn^{3+}

Lab-made reference
Birnessite, [Zn]/[Mn]=0.008



Tetrahedral and some octahedral Zn, with Mn^{3+}

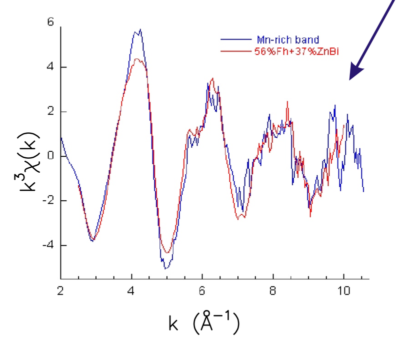
Zn EXAFS: Japan



EXAFS differs from place to place, unlike in Baltic nodule.

Fit of Mn-rich spot consistent with mixture of Zn-sorbed ferrihydrite (Note: XRD finds 6-line Fh) and Zn-sorbed birnessite (similar to Baltic).

Fit of Fe-rich area not yet clear. Possible phosphate component.

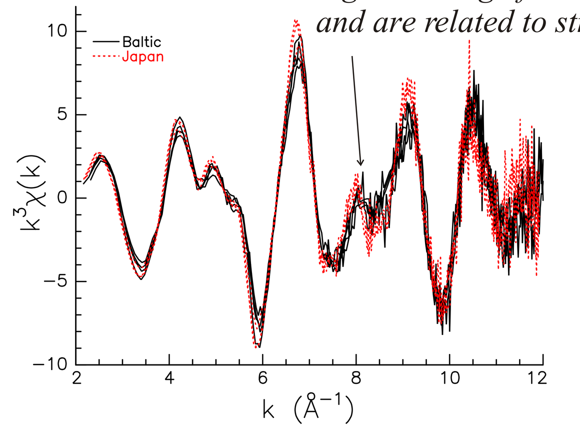


Zn in Japan sample is coordinated to ferrihydrite, birnessite, and at least one other species, in proportions depending on Fe/Mn ratios.

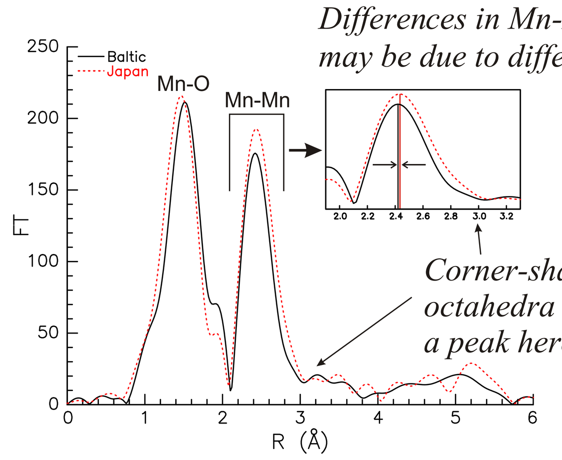
Mn EXAFS

Comparison of Baltic and Japan

Differences in this region are significant and are related to structure



Differences in Mn-Mn distances may be due to different [Mn^{3+}]



Corner-sharing Mn-O octahedra would cause a peak here

Mn EXAFS from the two samples look mostly alike, but with differences. Analysis shows:

Baltic: Turbostratic (from XRD) birnessite with some Mn^{3+}

Japan: Consistent with mixture of birnessite and lithiophorite. Slight Mn-Mn distance expansion suggesting more Mn^{3+} in layer than in Baltic.

Both: Uniform over several spots of varying composition.